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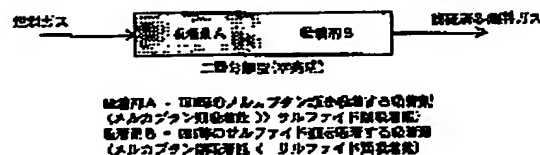
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(54) DESULFURIZER FOR FUEL GAS AND METHOD FOR DESULFURIZATION

(57)Abstract:

PROBLEM TO BE SOLVED: To simultaneously and efficiently adsorbing and removing sulfur compounds in a fuel gas containing at least both mercaptans such as TBM and the like and sulfides such as DMS and the like by one desulfurizer.

SOLUTION: This desulfurizer for fuel gas is provided by filling adsorbents having different sulfur-adsorptivity on the upstream side and the down stream side of a vessel for desulfurization or mixing two or more species of adsorbents having different sulfur compound-adsorptivity and filling the mixture. This method for desulfurization is to use the desulfurizer. As a species of the adsorbent having different sulfur compound-adsorptivity, 'the adsorbent in which one or more species of transition metals selected from Ag, Cu, Zn, Fe, Co and Ni are supported on a zeolite of X type, Y type or β type by ion-exchange' is preferably used.



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CLAIMS

[Claim(s)]

[Claim 1] The desulfurizing plant of the fuel gas characterized by coming to fill up the adsorbent with which it is the desulfurizing plant of sulfur compound content fuel gas, and sulfur compound adsorption capacity differs by the upstream and downstream in a desulfurization container.

[Claim 2] The desulfurizing plant of the fuel gas characterized by mixing two or more sorts of adsorbents with which it is the desulfurizing plant of sulfur compound content fuel gas, and sulfur compound adsorption capacity differs in a desulfurization container, and coming to be filled up.

[Claim 3] The desulfurizing plant of the fuel gas which is the desulfurizing plant of sulfur compound content fuel gas, and is characterized by filling up the upstream with the existing sulfur compound adsorbent, and coming to fill up the sulfur compound adsorbent which makes it come to support one sort or two sorts or more of transition metals chosen as the zeolite from Ag, Cu, Zn, Fe, Co, and nickel by the downstream according to the ion exchange into a desulfurization container.

[Claim 4] The desulfurizing plant of the fuel gas characterized by mixing the sulfur compound adsorbent which makes it come to support one sort or two sorts or more of transition metals which are the desulfurizing plants of sulfur compound content fuel gas, and were chosen as an existing sulfur compound adsorbent and an existing zeolite from Ag, Cu, Zn, Fe, Co, and nickel into the desulfurization container according to the ion exchange, and coming to be filled up.

[Claim 5] The desulfurizing plant of the fuel gas according to claim 3 to 4 characterized by the above-mentioned existing sulfur compound adsorbent being activated carbon.

[Claim 6] The desulfurizing plant of the fuel gas according to claim 3 to 5 characterized by the above-mentioned zeolite being an X type zeolite, Y mold zeolite, or beta mold zeolite.

[Claim 7] The desulfurizing plant of the fuel gas according to claim 1 to 6 whose above-mentioned sulfur compound content fuel gas is fuel gas which contains mercaptans and sulfide at least.

[Claim 8] The desulfurizing plant of the fuel gas according to claim 1 to 7 whose above-mentioned sulfur compound content fuel gas is town gas, LP gas, or natural gas.

[Claim 9] The desulfurization approach of the fuel gas characterized by letting pass and desulfurizing two or more sorts of adsorbents with which it comes to fill up the adsorbent with which it is the desulfurization approach of sulfur compound content fuel gas, and sulfur compound adsorption capacity differs this fuel gas by the upstream and downstream in a desulfurization container, or sulfur compound adsorption capacity differs to the desulfurizing plant which it mixes and comes to fill up.

[Claim 10] The desulfurization approach of the fuel gas characterized by letting pass and desulfurizing to the desulfurizing plant which comes to fill up the sulfur compound adsorbent which it is [adsorbent] the desulfurization approach of sulfur compound content fuel gas, and makes it come to support one sort or two sorts or more of transition metals which filled up the upstream with the existing sulfur compound adsorbent into the desulfurization container, and were chosen as the zeolite from Ag, Cu, Zn, Fe, Co, and nickel by the downstream in this fuel gas according to the ion exchange.

[Claim 11] The desulfurization approach of the fuel gas characterized by letting pass and

desulfurizing the sulfur compound and adsorbent which makes it come to support one sort or two sorts or more of transition metals which are the desulfurization approaches of sulfur compound content fuel gas, and were chosen as an existing sulfur compound adsorbent and an existing zeolite from Ag, Cu, Zn, Fe, Co, and nickel into the desulfurization container in this fuel gas according to the ion exchange to the desulfurizing plant which it mixes and comes to fill up.
[Claim 12] The desulfurization approach of the fuel gas according to claim 10 to 11 characterized by the above-mentioned zeolite being an X type zeolite, Y mold zeolite, or beta mold zeolite.
[Claim 13] The desulfurization approach of fuel gas according to claim 9 to 12 that the above-mentioned sulfur compound content fuel gas is fuel gas which contains mercaptans and sulfide at least.
[Claim 14] The desulfurization approach of fuel gas according to claim 9 to 13 that the above-mentioned sulfur compound content fuel gas is town gas, LP gas, or natural gas.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the approach of carrying out adsorption treatment of the desulfurizing plant for carrying out adsorption treatment of the sulfur compound in fuel gas, such as a desulfurizing plant of fuel gas and the desulfurization approach, i.e., town gas, and LP gas, and the sulfur compound in these fuel gas, and desulfurizing fuel gas.

[0002]

[Description of the Prior Art] It is used as fuels, such as industrial use and home use, and also gas, such as low-grade hydrocarbon gas, such as methane, ethane, ethylene, a propane, and butane, or natural gas containing these, town gas, and LP gas, is used as a raw material for manufacture of the hydrogen used as the fuel for fuel cells, a controlled atmosphere, etc. In the steam reforming process which is one of the industrial manufacture approaches of hydrogen, under existence of catalysts, such as nickel system and Ru system, a steam is added, those low-grade hydrocarbon gas is reformed, and the reformed gas which uses hydrogen as a principal component is generated.

[0003] As odorant aiming at leakage security, sulfur compounds, such as sulfide, and thiophenes or mercaptans, are contained in fuel gas, such as town gas and LP gas. Specifically, they are tertiary butyl mercaptan (similarly it is called TBM for short), an isopropyl mercaptan, a normal propyl mercaptan, tertiary amyl mercaptan, a tertiary heptyl mercaptan, methyl mercaptan, ethyl mercaptan, etc. as tetrahydrothiophene (similarly it is called THT for short) and mercaptans as sulfide as dimethyl sulfide (it calls for short the inside DMS of this description), ethyl methyl sulfide, diethyl sulfide, and thiophenes.

[0004] Many DMS, THT, and TBM are used as odorant generally added, and each of the concentration is several ppm. In town gas, the case using both DMS and TBM is almost especially the case. For example, poisoning of the catalyst used with said steam reforming process will be carried out with these sulfur compounds, and it will cause performance degradation. For this reason, it is necessary to remove those sulfur compounds in fuel gas from fuel gas beforehand. Moreover, as for the amount of the residual sulfur compound, it is desirable for the residual sulfur compound also of little ** rare ***** to be low concentration as much as possible even if in the fuel gas which removed the sulfur compound.

[0005] Conventionally, the hydrodesulfurization process and the approach by the adsorbent are learned as the clearance approach of the sulfur compound contained in fuel gas. although add hydrogen to fuel gas, make a sulfur compound disassemble into a hydrogen sulfide under existence of catalysts, such as a Co-Mo system catalyst, and the hydrogen sulfide which is a decomposition product is made to stick to devulcanizing agents, such as a zinc oxide and an iron oxide, and being desulfurized, addition and heating of hydrogen are required of a hydrodesulfurization process -- etc. -- desulfurization actuation is dramatically complicated. On the other hand, the approach by the adsorbent is the approach of making adsorb a sulfur compound and removing by making the adsorbent which uses activated carbon, a metallic oxide, or a zeolite as a principal component pass fuel gas.

[0006] Although there is also an approach to which the adsorption capacity force is made to

increase by heating among approaches by the adsorbent, since a system becomes simpler [direction] making it adsorb in ordinary temperature, it is desirable. Since the method of removing a sulfur compound in ordinary temperature using an adsorbent needs neither heat nor hydrogen like a hydrodesulfurization process or a heating adsorption process, it is the simple desulfurization approach. This adsorbent is filled up with and used for a desulfurization container as shown in drawing 1 . However, since it becomes impossible to remove the sulfur compound in gas when an adsorbent is saturated with the sulfur compound by which this was adsorbed, playback and exchange are required. Therefore, since the initial complement of an adsorbent and exchange frequency will be greatly influenced by the size of the adsorption capacity force of an adsorbent, an adsorbent which has the higher adsorption capacity force is desired.

[0007] Since the ordinary temperature desulfurization process using adsorbents, such as activated carbon, and a manganese dioxide, a zeolite, only lets fuel gas pass to an adsorbent, it is a very simple approach. However, in the case of the adsorbent of these existing, especially the engine performance is influenced by the property of a sulfur compound. That is, the existing ordinary temperature adsorbents, such as activated carbon, and a manganese dioxide, a zeolite, do not have the enough adsorption engine performance, and its adsorption engine performance of sulfide, such as DMS, is especially low.

[0008] Various adsorbents are proposed as an adsorbent of the sulfur compound in gas until now. For example, in JP,6-306377,A, the mercaptans which are the odorization components of fuel gas, such as town gas and LP gas, are selectively said that polyvalent metal ion-exchange zeolites other than hydrogen and/or alkaline earth metal remove under an anoxia ambient atmosphere, a zeolite here is used regardless of the class, and it is supposed that Mn, Fe, Co, nickel, Cu, Sn, and Zn are desirable as polyvalent metal ion. The sulfur compounds for adsorption in this technique are only the easy mercaptans of adsorption, and the check of that adsorption capacity is performed by introducing 350 ppm TBM (town gas balance) into the sampling bag which put the above-mentioned zeolite into that example as the publication.

[0009] Moreover, in the manufacture process or a supply process, the case where the moisture of a minute amount is contained is in fuel gas. Although the selectivity which is not concerned with the existence of the moisture in fuel gas, but adsorbs a sulfur compound is required, in the conventional adsorbent, nothing is considered about this point including the adsorbent of the above-mentioned official report. In addition, about sulfide, such as mercaptans, such as TBM used as odorant in many cases, and DMS, since it is harder to adsorb in sulfide, such as DMS, especially in the conventional adsorbent, it becomes very important to make the amount of adsorption of sulfide, such as DMS, increase.

[0010] this invention person etc. is effective regardless of the class of sulfur compound, even if moisture is contained in fuel gas, as a result of pursuing about the adsorbent which functions still more effectively and continuing various experiments and examination from these many viewpoints, even if moisture was contained in fuel gas. Also about sulfide, such as DMS, the sulfur compound adsorbent in the fuel gas which has the outstanding adsorption capacity was developed previously, and it has applied [an application for patent 2000-23955 (application for patent 2000-232780), an application for patent 2000-123527, and an application for patent 2000-256493].

[0011] Although this adsorbent makes it come to support one sort or two sorts or more of transition metals chosen as the zeolite from Ag, Cu, Zn, Fe, Co, and nickel according to the ion exchange and has the adsorption engine performance regardless of the class of sulfur compounds, such as sulfide, thiophenes, and mercaptans, it has the adsorption engine performance which was especially excellent about sulfide, such as DMS. In this point, conventional activated carbon and a manganese dioxide, or a zeolite, since the adsorption engine performance of DMS is low, the above-mentioned adsorbent can be called unique adsorbent.

[0012]

[Problem(s) to be Solved by the Invention] This invention aims at offering the approach of being more [being simultaneous and] efficient, carrying out adsorption treatment of the sulfide, such as mercaptans, such as TBM, and DMS, out of a desulfurizing plant as it is more [being simultaneous and] efficient in sulfide, such as mercaptans, such as fuel gas, such as town gas,

and LP gas, natural gas, toluene, and DMS, and comes to carry out adsorption treatment, and these fuel gas, and desulfurizing fuel gas by using the above data.

[0013]

[Means for Solving the Problem] This invention is the desulfurizing plant of (1) sulfur-compound content fuel gas. In a desulfurization container The desulfurizing plant of the fuel gas characterized by coming to fill up with the upstream and downstream the adsorbent with which sulfur compound adsorption capacity differs is offered. Moreover, this invention is the desulfurizing plant of (2) sulfur-compound content fuel gas, and the desulfurizing plant of the fuel gas characterized by mixing two or more sorts of adsorbents with which sulfur compound adsorption capacity differs in a desulfurization container, and coming to be filled up is offered.

[0014] The desulfurizing plant of the fuel gas characterized by this invention being the desulfurizing plant of (3) sulfur-compound content fuel gas, and coming to fill up the sulfur compound adsorbent which makes it come to support one sort or two sorts or more of transition metals which filled up the upstream with the existing sulfur compound adsorbent into the desulfurization container, and were chosen as the zeolite from Ag, Cu, Zn, Fe, Co, and nickel by the downstream according to the ion exchange is offered.

[0015] The desulfurizing plant of the fuel gas characterized by this invention mixing the sulfur compound adsorbent which makes it come to support one sort or two sorts or more of transition metals which are the desulfurizing plants of (4) sulfur-compound content fuel gas, and were chosen as an existing sulfur compound adsorbent and an existing zeolite from Ag, Cu, Zn, Fe, Co, and nickel into the desulfurization container according to the ion exchange, and coming to be filled up is offered.

[0016] Moreover, this invention is the desulfurization approach of sulfur compound content fuel gas, and offers the desulfurization approach of the fuel gas characterized by desulfurizing through this fuel gas to the desulfurizing plant of above-mentioned (1) - (4).

[0017]

[Embodiment of the Invention] In this invention, the desulfurizing plant which mixes the adsorbent with which it is filled up with the adsorbent with which sulfur compound adsorption capacity differs by the upstream and downstream in a desulfurization container in the flow direction of processed sulfur compound content fuel gas, or sulfur compound adsorption capacity differs, and it comes to fill up is used. And adsorption treatment of two or more sulfur compounds contained in fuel gas can be simultaneously carried out with one desulfurizing plant by making both adsorbents contact through sulfur compound content fuel gas into the desulfurizing plant filled up with both adsorbents in this way.

[0018] This invention is applied to desulfurization of the fuel gas which contains both sulfide, such as mercaptans, such as TBM, and DMS, at least especially. As a kind of the adsorbents with which the above-mentioned sulfur compound adsorption capacity in this invention differs, the existing sulfur compound adsorbents, such as metallic oxides, such as activated carbon and a manganese dioxide, or a zeolite, can be used, for example. Generally as for these adsorbents, high adsorption capacity is shown to a sulfur compound with the high boiling point. In Above TBM (64.4 degrees C of boiling points), and DMS (37.2 degrees C of boiling points), the adsorption capacity to TBM is high. Therefore, although metallic oxides, such as activated carbon which is the existing sulfur compound adsorbent, and a manganese dioxide, a zeolite, etc. are effective in adsorption of mercaptans, such as TBM, they are not effective in adsorption of sulfide, such as DMS.

[0019] On the other hand, as other kinds of the adsorbent with which said sulfur compound adsorption capacity differs, the high adsorbent of especially adsorption capacity is used among the sulfur compounds in fuel gas to the sulfide of the sulfide, such as mercaptans, such as the specific component to which it is hard to stick, i.e., TBM etc., and DMS, such as DMS, with the above-mentioned existing sulfur compound adsorbent.

[0020] Although all will be used if it is the adsorbent which has such engine performance as a high adsorbent of especially adsorption capacity to sulfide, such as DMS, the sulfur compound adsorbent concerning the above-mentioned application for patent 2000-23955 (application for patent 2000-232780), an application for patent 2000-123527, and an application for patent 2000-

256493 can be mentioned as a desirable example. These are previously developed by this invention persons.

[0021] The above-mentioned sulfur compound adsorbent is an adsorbent which makes a zeolite come to support one sort or two sorts or more of transition metals chosen from Ag, Cu, Zn, Fe, Co, and nickel according to the ion exchange, and all cannot be concerned with the moisture concentration in fuel gas, but, in addition to thiophenes, such as sulfide, such as mercaptans, such as TBM contained in fuel gas, and DMS, and THT, can remove a hydrogen sulfide etc. effectively. Especially the adsorbent that made Ag or Cu support also in these transition metals is effective. As a zeolite, an X type zeolite, Y mold zeolite, and beta mold zeolite are used preferably.

[0022] In order to manufacture the above-mentioned adsorbent, each transition metals chosen from Above Ag, Cu, Zn, Fe, Co, and nickel are made to support by the ion-exchange method to a zeolite first. The compound of these metals is dissolved in water and, specifically, it considers as a water solution. As a compound of each metal, in order to carry out the ion exchange to the cation of a zeolite, it dissolves in water and the metallic compounds with which a metal may exist as a metal ion are used among the water solution. The cation in a zeolite is made to exchange for these metal ions by contacting this water solution with the ** agitating method, ** impregnation method, ** flow method, etc., as shown in a zeolite and below-mentioned drawing 4. Subsequently, after washing with water etc., it dries and is obtained by calcinating if needed.

[0023] The above-mentioned adsorbent for sulfur compound clearance can apply one sort or two sorts or more of sulfur compounds of the above-mentioned sulfide in [various] fuel gas, thiophenes, and the mercaptans to carrying out adsorption treatment. In addition to these sulfur compounds, this adsorbent acts effective also in adsorption treatment, such as a hydrogen sulfide, but it has the adsorption capacity which was especially excellent about sulfide, such as DMS. For this reason, it can be used suitable to carry out adsorption treatment of these sulfur compounds from fuel gas, such as town gas and LP gas, especially.

[0024] in this invention, adsorption treatment of both sulfide, such as mercaptans, such as TBM contained in fuel gas, such as town gas, and DMS, can be carried out that it is simultaneous and more efficiently with one desulfurizing plant by using the high adsorbent of especially adsorption capacity to sulfide, such as above DMS, with said existing adsorbent (that is, the existing adsorbent -- doubling). The desulfurizing plant which comes to carry out mixed filling of the adsorbent with which the adsorbent with which sulfur compound adsorption capacity differs is filled up with the upstream and downstream into a desulfurization container as a desulfurizing plant, or sulfur compound adsorption capacity differs is used. Drawing 2 -3 are drawing showing the example of a mode of the desulfurizing plant of this invention.

[0025] Drawing 2 is the case of the desulfurizing plant which comes to fill up with the upstream and downstream two kinds of adsorbents with which sulfur compound adsorption capacity differs into a desulfurization container. Adsorbent A is an adsorbent (mercaptans adsorption-capacity >> sulfide adsorption capacity: > shows the superiority or inferiority of adsorption capacity, and the number shows extent of the superiority or inferiority.) which adsorbs mercaptans, such as TBM. the following -- being the same -- a desulfurization container Nakagami style side is filled up. Adsorbent B is an adsorbent (mercaptans adsorption capacity < sulfide adsorption capacity) which sticks to sulfide, such as DMS, and a desulfurization container Nakashita style side is filled up with it.

[0026] Although the above-mentioned mode (drawing 2) is the so-called bilayer discrete type with which the upstream is filled up with Adsorbent A and it fills up the downstream with Adsorbent B In using "the adsorbent which makes a zeolite come to support one sort or two sorts or more of transition metals chosen from Ag, Cu, Zn, Fe, Co, and nickel according to the ion exchange" especially as an adsorbent B Even if only the case of the bilayer discrete type of restoration sequence "the adsorbent A-> adsorbent B" is effective and is the same bilayer discrete type, with the bilayer discrete type of restoration sequence "the adsorbent B-> adsorbent A", the effectiveness of this invention is not acquired from the upstream. Although this reason is unknown, in the bilayer discrete type of the adsorbent A-> adsorbent B, it is thought that a certain different significant absorption from the absorption in the bilayer discrete

type of the adsorbent B-Adsorbent A has occurred.

[0027] Drawing 3 is the case of the desulfurizing plant which mixes two or more sorts of adsorbents with which sulfur compound adsorption capacity differs, and it comes to fill up into a desulfurization container. Adsorbent A is an adsorbent (mercaptans adsorption capacity < sulfide adsorption capacity) which sticks to sulfide, such as DMS, and into a desulfurization container, the adsorbent (mercaptans adsorption capacity >> sulfide adsorption capacity) which adsorbs mercaptans, such as TBM, and Adsorbent B mix both adsorbents, and are filled up with it. Stainless steel, glass, various plastics, etc. are mentioned that what is necessary is just the ingredient which is not invaded by processed fuel gas as a component of the desulfurization container of this invention.

[0028] In these desulfurizing plants, as an adsorbent B, if the sulfur compound adsorbent which makes it come to support one sort or two sorts or more of transition metals chosen from Ag, Cu, Zn, Fe, Co, and nickel according to the ion exchange is used for the zeolite of either a zeolite especially said X type zeolite, Y mold zeolite and beta mold zeolite, in addition to mercaptans and sulfide, adsorption treatment also of the sulfur compounds, such as thiophenes and a hydrogen sulfide, can be simultaneously carried out to it from fuel gas. Although the existing sulfur compound adsorbents, such as metallic oxides, such as activated carbon and a manganese dioxide, or a zeolite, are used as an adsorbent A, for example in that case, activated carbon is used especially preferably.

[0029]

[Example] Hereafter, although this invention is explained in more detail based on an example, of course, this invention is not restricted according to these examples.

[0030] <preparation of a sample offering adsorbent> -- the Na-X mold zeolite (the TOSOH CORP. make --) of marketing as a zeolite trade name: -- F9-HA and SiO₂/aluminum₂O₃ ratio (the same a mole ratio and the following) -- =2.5 -- a commercial H-beta mold zeolite (the TOSOH CORP. make and trade name:HSZ -- 930 HOD) SiO₂/aluminum₂O₃ ratio -- =27.4 and a commercial Na-Y mold zeolite (the TOSOH CORP. make --) trade name: -- HSZ320NAD and SiO₂/aluminum₂O₃ ratio -- =5.7 -- a commercial H-Y mold zeolite (the TOSOH CORP. make and trade name:HSZ -- 320 HOD) SiO₂/aluminum₂O₃ ratio -- =5.6 and a H-USY mold zeolite (the TOSOH CORP. make --) trade name: -- HSZ360HUD and SiO₂/aluminum₂O₃ ratio -- =13.7 -- The K-L mold zeolite (the TOSOH CORP. make, trade name:HSZ500KOD, SiO₂/aluminum₂O₃ ratio = 6.0) and Na-mordenite mold zeolite (the TOSOH CORP. make, trade name:HSZ642NAD, SiO₂/aluminum₂O₃ ratio = 18.3) were used.

[0031] These zeolites are fabricated on a cylindrical pellet (the diameter of 1.5mm, die length = 3-4mm), using an alumina or about clay 20wt% as a binder. On the other hand, a silver nitrate, copper acetate, etc. were dissolved in distilled water, and the water solution of each metal salt was obtained. By the various ion-exchange approaches shown in drawing 4 using the water solution of each [these] metal salt, after making each cation in the above-mentioned zeolite (Na⁺, K⁺, or H⁺) exchange for Ag ion, Cu ion, Zn ion, Fe ion, Co ion, and nickel ion, distilled water (inside DIW of drawing 4) washed 5 times, and, subsequently it dried and calcinated.

[0032] These results are collectively shown in a table 1. Among a table 1, although the code shows to the column of a sample name, among this column, although "Ag(Na)-Y" made the Na-Y mold zeolite support Ag according to the ion exchange, it is semantics, and the same is said of this point, a table 2, and the following publications. In addition, desiccation and baking conditions are common, and each sample performed desiccation at 100 degrees C into air on the 1st, and performed baking at 400 degrees C into desiccation nitrogen for 2 hours. In this way, each sample offering adsorbent which made various zeolites support a metal according to the ion exchange was obtained.

[0033]

[Table 1]

サンプル名	ゼオライト重量 /g	試薬	試薬 /g	蒸留水 /g	イオン交換方法
Ag (Na)-Y	30	硝酸銀	22.9	500	攪拌法
Ag (O)-Y	50	硝酸銀	31.1	500	攪拌法
Ag (Na)-X	75	硝酸銀	30.6	800	攪拌法
Ag (O)-β	30	硝酸銀	11.0	150	含浸法
Cu (O)-Y	75	酢酸銅1水和物	20.5	800	攪拌法
Cu (Na)-X	75	酢酸銅1水和物	17.9	800	攪拌法
Cu (O)-β	30	酢酸銅1水和物	6.9	150	含浸法
Zn (O)-β	30	硫酸亜鉛7水和物	9.4	150	含浸法
Fe (O)-β	30	硫酸鉄7水和物	4.8	500	攪拌法
Co (O)-β	30	酢酸コバルト4水和物	4.4	150	含浸法
Ni (O)-β	30	酢酸ニッケル4水和物	4.4	150	含浸法
Na (O)-β	30	塩化ナトリウム	20.3	500	攪拌法
Ag (O)-USY	50	硝酸銀	14.4	500	攪拌法
Ag (O)-L	30	硝酸銀	21.9	500	攪拌法
Ag (Na)-Mor	30	硝酸銀	8.5	150	含浸法

[0034] <An example 1 - the examples 1-17 of 13:comparison> (sulfur compound adsorption test 1)

The adsorption test of a sulfur compound was carried out using the testing device shown in drawing 5. The packed tube (cylinder coil) was filled up with each sample offering adsorbent obtained above among drawing 5, and the adsorption test of a sulfur compound was carried out about each. The test condition was carried out as follows. Packed tube: 28.4mm(diameter) x63.2mm (height) and this were filled up with 3 40cm of each sample offering adsorbent. trial gas: -- town gas [13A:methane ** -- 87.8% (the same, when it cannot touch capacity % and especially the following) Ethane **5.9%, propane **4.6%, n-butane **0.8%, and i-butane **0.8%], sulfur compound concentration [in trial gas]: -- 4.4 mg-SNm3 (DMS=50wt% --) This added 380 ppm (-30 degrees C of dew-points) of **** TBM=50wt% in this gas equivalent to DMS=1.8ppm (it is the same capacity ppm and the following) and TBM=1.2ppm (based on underwater bubbling of the trial gas in the inside of a thermostat). Gas rate: 340 L/h, LV(linear velocity of gas) =15 cm/sec, SV(space velocity) =8500h-1, a temperature:room temperature (20 degrees C), pressure:ordinary pressure. This adsorption test was altogether carried out on the same equipment and the same conditions including the example of a comparison.

[0035] The amount of adsorption of the sulfur compound by each sample offering adsorbent was carried out as follows, and was calculated. By the above-mentioned test condition, trial gas was introduced from the packed tube inlet port, the gas discharged from a packed tube outlet was sampled with time, and it asked for the concentration of a sulfur compound by GC-FPD (gas chromatograph with a flame photometric detector). The amount of adsorption of a sulfur compound integrates the total sulfur compound amount of adsorption of the event of each sulfur compound concentration in a packed tube outlet amounting to 0.1 ppm, and computes it as the sulfur amount of adsorption by the following formula (1). The same is said of this point and the following examples.

[0036]

[Formula 1]

$$\text{硫黄吸着量 (wt\%)} = \frac{\text{吸着した硫黄化合物中の硫黄量 (g)}}{\text{吸着剤の重量 (g)}} \times 100 \quad (1)$$

[0037] A table 2 is as a result of the above-mentioned adsorption test. The result of having made it the same with the above and having performed the adsorption test about the various porous materials considered having the various adsorbents and absorption of marketing besides the various commercial zeolite itself as an example of a comparison is also shown in a table 2.

[0038]

[Table 2]

例番号	サンプル名	担持材料	Si/Al ₂	吸着剤名(商品名等)	元	硫黄吸着量
実施例1	Ag(OH)-Y	Na-Y型ゼオライト	5.7	HSZ320RAD	東ソー	4.10wt%
実施例2	Ag(OH)-Y	H-Y型ゼオライト	5.6	HSZ320HOD	東ソー	1.91wt%
実施例3	Ag(OH)-X	Na-X型ゼオライト	2.5	F9-HA	東ソー	1.73wt%
実施例4	Ag(OH)-β	H-β型ゼオライト	27.4	HSZ390HOD	東ソー	1.70wt%
実施例5	Ag(OH)-USY	H-USY型ゼオライト	13.7	HSZ350HOD	東ソー	0.34wt%
実施例6	Ag(OH)-L	K-L型ゼオライト	6.0	HSZ500KOD	東ソー	0.19wt%
実施例7	Ag(Na)-Mor	Na-モルデナイト型ゼオライト	18.3	HSZ642HAD	東ソー	0.46wt%
実施例8	Cu(OH)-Y	H-Y型ゼオライト	5.6	HSZ320HOD	東ソー	1.17wt%
実施例9	Cu(OH)-β	H-β型ゼオライト	27.4	HSZ390HOD	東ソー	1.10wt%
実施例10	Zn(OH)-β	H-β型ゼオライト	27.4	HSZ390HOD	東ソー	0.24wt%
実施例11	Fe(OH)-β	H-β型ゼオライト	27.4	HSZ390HOD	東ソー	0.14wt%
実施例12	Co(OH)-β	H-β型ゼオライト	27.4	HSZ390HOD	東ソー	0.14wt%
実施例13	Ni(OH)-β	H-β型ゼオライト	27.4	HSZ390HOD	東ソー	0.13wt%
比較例1	Na-Y	Na-Y型ゼオライト	5.7	HSZ320HAD	東ソー	<0.01wt%
比較例2	H-Y	H-Y型ゼオライト	5.6	HSZ320HOD	東ソー	0.05wt%
比較例3	Na-X	Na-X型ゼオライト	2.5	F9-HA	東ソー	0.23wt%
比較例4	H-β	H-β型ゼオライト	27.4	HSZ390HOD	東ソー	0.06wt%
比較例5	Na-β	H-β型ゼオライト	27.4	HSZ390HOD	東ソー	0.04wt%
比較例6	H-USY	H-USY型ゼオライト	13.7	HSZ350HOD	東ソー	<0.01wt%
比較例7	K-L	K-L型ゼオライト	6.0	HSZ500KOD	東ソー	<0.01wt%
比較例8	Na-Mor	Na-モルデナイト型ゼオライト	18.3	HSZ642HAD	東ソー	0.01wt%
比較例9	H-Mor	H-モルデナイト型ゼオライト	15.0	HSZ620HOD	東ソー	<0.01wt%
比較例10	活性炭	活性炭(ハロゲン吸着用)		XRC824	武田薬品	0.03wt%
比較例11	活性炭	活性炭(硫黄吸着用)		TAC824	武田薬品	0.03wt%
比較例12	活性炭	活性炭(付臭剤吸着用)		SRCA	武田薬品	0.07wt%
比較例13	金属酸化物	ZnO		C7-2	東洋CC	—
比較例14	アルミナ	活性アルミナ		KHD12	住友化学	0.01wt%
比較例15	アルミナ	活性アルミナ		KHO12	住友化学	—
比較例16	シリカ	シリカゲル		A型	富士シリシア化学	0.08wt%
比較例17	シリカ	シリカゲル		B型	富士シリシア化学	<0.01wt%

(備考) ①Si/Al₂はSiO₂/Al₂O₃モル比。②硫黄吸着量の欄で「—」のものは、試験開始直後から硫黄化合物の吸着が始まったもので、実質上硫黄化合物の吸着能はないことを示している。

[0039] As a table 2, in a thing with a commercial zeolite (examples 1-9 of a comparison), even if the sulfur amount of adsorption is good, it is 0.23wt(s)%. Moreover, about adsorbents other than a commercial zeolite (examples 10-17 of a comparison), it is lower than it. That is, if adsorbents, such as a commercial zeolite and activated carbon, remain as they are, they show that it is not useful as an adsorbent of the sulfur compound in the fuel gas containing moisture.

[0040] On the other hand, although examples 1-13 are the cases where a commercial zeolite is made to support transition metals, such as Ag, Cu, Zn, Fe, Co, and nickel, according to the ion exchange, compared with the thing with a commercial zeolite, the sulfur adsorption engine performance is improved effectively. Especially the sulfur amount of adsorption at the time of making an X type zeolite, Y mold zeolite, and beta mold zeolite support silver or copper according to the ion exchange (examples 1-4, 8-9) exceeds 1wt%, and shows the very effective adsorption property. Especially the sulfur amount of adsorption at the time of making a Na-Y mold zeolite support Ag according to the ion exchange especially (example 1) indicates the outstanding adsorption property to be 4.1wt(s)%. Although 1.8 ppm and 1.2 ppm of TBM are contained in trial gas for DMS and about 380 ppm of water are contained in it, DMS and TBM are effectively adsorbed under coexistence of such moisture.

[0041] <Example 14> (sulfur-compound adsorption test 2: adsorption performance test classified by class of a sulfur compound)

The following adsorbent A and Adsorbent B were prepared as an adsorbent.

Adsorbent A: Commercial activated carbon for desulfurization (the Takeda Chemical Industries, Ltd. make, the granular egret NCC)

Adsorbent B: The adsorbent of an example 1 (what carried out the ion exchange of the complex ion to the Na-Y mold zeolite in the silver-nitrate water solution)

Using the testing device shown in drawing 5, tales-doses restoration of these adsorbents A and the adsorbent B was carried out at the packed tube [a quartz tube with a bore of 8mm (inner diameter)], respectively, and the adsorption test was carried out for every class of sulfur compound. Adsorbent B was filled up with what ground the pellet of the cylindrical shape obtained above <preparation of a sample offering adsorbent>, and carried out the particle size regulation to the range of 0.35 to 0.71mm three times 1.0cm. The particle size regulation of the

adsorbent A was carried out with the same particle size, and it was used for it. As trial gas, each gas which carried out about 1000 ppm (-20 degrees C of dew-points) addition of the water was used for each gas (respectively 10 ppm, N2 balance) which diluted DMS, TBM, THT, CS2, H2S, and CH3SH with nitrogen, respectively. The gas flow rate set to 1000cm³/min (SV=60000h⁻¹), sampled the gas of an adsorbent layer outlet side with time, measured it with the fixed time interval by GC-FPD, and asked for the concentration of each sulfur compound.

[0042] Drawing 6 is as a result of the above-mentioned adsorption test. It turns out as drawing 6 that the sulfur adsorption engine performance of Adsorbent B is excellent compared with the sulfur adsorption engine performance of Adsorbent A. the adsorption engine performance which especially the adsorbent A boiled Adsorbent B markedly to not being [to which it sticks slightly] alike too much (sulfur amount of adsorption = 0.7wt%), and was excellent about DMS is shown (sulfur amount of adsorption = 4.9wt%). About TBM, although it is a both **** EQC, Adsorbent B shows [SH / THT, H2S, and / CH3] the adsorption engine performance which was excellent compared with Adsorbent A.

[0043] <Example 15> (sulfur compound adsorption test 3: adsorption performance test of TBM and DMS)

About same Adsorbent A and same Adsorbent B as having used in the example 14, the breakthrough situation according to sulfur compound of TBM and DMS was measured. As trial gas, the gas which carried out about 1000 ppm (-20 degrees C of dew-points) addition of the water was used for the gas (DMS=5ppm, TBM=5ppm, N2 balance) which diluted TBM and DMS with nitrogen. The gas flow rate set to 1000cm³/min (SV=60000h⁻¹), sampled the gas of an adsorbent layer outlet side with time, measured it with the fixed time interval by GC-FPD, and asked for the concentration of TBM and DMS.

[0044] Drawing 7 is as a result of this adsorption test. Drawing 7 (a) Time amount until a breakthrough appears about TBM has long Adsorbent A compared with Adsorbent B as - (b). On the other hand, to carrying out a breakthrough at the time of about 300-minute progress, with Adsorbent B, a breakthrough does not appear till about 1200-minute progress, but the adsorption engine performance is maintained about DMS with Adsorbent A.

[0045] <Example 16> (sulfur-compound adsorption test 4: the method [Adsorbent / C / Adsorbent A, Adsorbent B, or] of restoration adsorption performance test by how)

The following adsorbent A, Adsorbent B, and Adsorbent C were prepared as an adsorbent.

Adsorbent A: Commercial activated carbon for desulfurization (the Takeda Chemical Industries, Ltd. make, the granular egret NCC)

Adsorbent B: The adsorbent of an example 1 (what carried out the ion exchange of the complex ion to the Na-Y mold zeolite in the silver-nitrate water solution)

Adsorbent C: The adsorbent of an example 4 (what carried out the ion exchange of the complex ion to the H-beta mold zeolite in the silver-nitrate water solution)

[0046] The adsorption test was carried out using the desulfurizing plant which changed and constituted the method [Adsorbent / in a desulfurization container / Adsorbent A, Adsorbent B, or Adsorbent C] of restoration. Drawing 8 is drawing showing restoration of the adsorbent A in the desulfurization container used by this adsorption test, and Adsorbent B, and arrangement relation. About Adsorbent C, it is the same as restoration of Adsorbent B, and arrangement relation. The desulfurizing plant with which drawing 8 (a) was filled up only with one kind each of Adsorbent A and Adsorbent B (single component type: example of a comparison), The desulfurizing plant with which drawing 8 (b) was filled up with Adsorbent A and Adsorbent B one by one from the fuel gas entrance side (bilayer discrete type: example), The desulfurizing plant (homogeneity hybrid model: example) with which drawing 8 (c) mixed Adsorbent A and Adsorbent B, and it was filled up, and drawing 8 (d) are the desulfurizing plants (bilayer discrete type: example of a comparison) filled up with Adsorbent B and Adsorbent A one by one from the fuel gas entrance side.

[0047] The above-mentioned desulfurization container was a tubular quartz tube, size was set to 8mm(inner diameter) x250mm (height), and capacity (capacity filled up with = adsorbent) was set to 3 1.0cm. It used by making Adsorbent A, Adsorbent B, and Adsorbent C into granularity with a diameter of 0.35-0.71mm. Drawing 8 (b) With the desulfurizing plant of - (d), the quantitative rate

of both adsorbent A and adsorbent B is equivalent weight (50% / 50%), every [0.5cm / 3]. %
The case where it is the same capacity % and the following, and Adsorbent A : it considered as
B= 25% of adsorbents, and 75% of case. Moreover, in arrangement of the bilayer discrete type
[what replaced with the adsorbent B in drawing 8 (b), and was filled up with Adsorbent C] of
Adsorbent A and Adsorbent C, they could be C= 50% of adsorbent A:adsorbents, and 50%.
[0048] The adsorption test replaced and carried out the packed tube part in drawing 5 with the
desulfurizing plant of above-mentioned drawing 8 (a) - (d) using the testing device shown in
drawing 5 at that time. The test condition was made the same with the above <an example 15>
(sulfur compound adsorption test 3: adsorption performance test of TBM and DMS), and
temperature was performed at the room temperature (25 degrees C), and was carried out at
least 50 degrees C with the bilayer discrete type of Adsorbent A and Adsorbent B. As a result, a
table 3 and drawing 9 -10 are.

[0049]

[Table 3]

	配置方法	配置		配合 (%)		硫黄吸着量 /wt%	温度 /℃
		上流	下流	上流	下流		
実施例	二層分離型	A	B	50	50	3.1	25
				25	75	3.6	
		A	C	50	50	2.0	
	均一混合型	A + B		A (50%) + B (50%)		2.8	50
		A + B		A (25%) + B (75%)		2.9	
	二層分離型	A	B	50	50	3.3	
				25	75	3.9	
比較例	単一成分型	A		100		1.0	25
		B		100		3.0	
		C		100		1.4	
	二層分離型	B	A	50	50	2.0	

吸着剤A 活性炭/武田NCC
吸着剤B Ag(Na)-Y
吸着剤C Ag(III)-β

[0050] In the desulfurizing plant which filled up only one kind each of Adsorbent A, Adsorbent B, and Adsorbent C with the conventional single component type [example: drawing 8 (aof comparison)], the adsorption engine performance of Adsorbent A, Adsorbent B, and each adsorbent C has appeared as it is first as a table 3. Next, the desulfurizing plant [example: drawing 8 (b)] filled up with Adsorbent A and Adsorbent B one by one from the trial gas inlet side shows the 3.1wt% amount of adsorption in the temperature of 25 degrees C a restoration rate, B= 50% of adsorbent A:adsorbents, and 50% with a bilayer discrete type, and it shows that TBM and DMS are adsorbed good.

[0051] On the other hand, with the desulfurizing plant [example: drawing 8 (dof comparison)] filled up with Adsorbent B and Adsorbent A one by one, it adsorbs only 2.0wt% in the same restoration rate and temperature with the same bilayer discrete type from this entrance side. Thus, the outstanding desulfurization effectiveness in the desulfurizing plant [example: drawing 8 (b)] filled up with Adsorbent A and Adsorbent B one by one from the trial gas inlet side concerning this invention is clear.

[0052] Furthermore, when temperature is raised at the temperature of 25 degrees C sulfur amount-of-adsorption 3.6wt% when it is made to B= 25% of adsorbent A:adsorbents, and 75% with the desulfurizing plant [example: drawing 8 (b)] which filled up Adsorbent A and Adsorbent B with the bilayer discrete type concerning this invention one by one from the entrance side as a table 3, and it is made 50 degrees C, the sulfur amount of adsorption is increasing further.

[0053] Moreover, the desulfurizing plant [example: drawing 8 (c)] which mixed and filled up Adsorbent A and Adsorbent B with the homogeneity hybrid model shows sulfur amount-of-adsorption 2.8wt% in the temperature of 25 degrees C a restoration rate, B= 50% of adsorbent A:adsorbents, and 50% as a table 3. When a restoration rate is changed and it considers as B=

25% of adsorbent A:adsorbent B and 75%, the sulfur amount of adsorption is increasing further.

[0054] Drawing 9 is drawing showing the method of restoration of the adsorbent A in a desulfurization container, and Adsorbent B, and the relation of the sulfur amount of adsorption. Among drawing 9, although the axis of abscissa is shown as mixing percentage [%] of Adsorbent B, when, as for a left end, Adsorbent B is filled up with 0% A, i.e., an adsorbent, a right end is the case where it is filled up with 100% B, i.e., an adsorbent. When equivalent restoration is carried out and it uses for the order of the adsorbent B→ adsorbent A about Adsorbent A and Adsorbent B, they are (** mark in drawing 9), and the 2.0wt% sulfur amount of adsorption.

[0055] On the other hand, when equivalent restoration is carried out and it uses for the order of the adsorbent A→ adsorbent B, (O mark in drawing 9) and the 3.1wt% sulfur amount of adsorption are shown, and when a restoration activity is carried out by the same order at B= 25% [of adsorbent A:adsorbents] : 75% of a rate, the 3.6wt% thing sulfur amount of adsorption is shown. Moreover, when mixed filling of Adsorbent A and the adsorbent B is carried out to equivalent homogeneity and they are used for it, (** mark in drawing 9 R> 9) and the 2.8wt% sulfur amount of adsorption are shown. thus, it turns out that it is markedly alike and the outstanding sulfur adsorption engine performance is obtained when it is filled up in order of the adsorbent A→ adsorbent B and uses compared with the case where it is filled up in order of the adsorbent B→ adsorbent A, and the sulfur adsorption engine performance which applies to this correspondingly when mixed filling of Adsorbent A and the adsorbent B is carried out and they are used is obtained.

[0056] Drawing 10 is a result at the time of carrying out mixed filling of Adsorbent A and Adsorbent C in a desulfurization container. Among drawing 10, although the axis of abscissa is shown as a mixing ratio [%] of Adsorbent C, when, as for a left end, Adsorbent C is filled up with 0% A, i.e., an adsorbent, a right end is the case where it is filled up with 100% B, i.e., an adsorbent. When mixed and filled up with Adsorbent A and Adsorbent C, compared with the case where Adsorbent A and Adsorbent C are used independently, it is shown that the sulfur amount of adsorption is improved intentionally.

[0057]

[Effect of the Invention] According to this invention, adsorption treatment of both the sulfur compounds in the fuel gas which contains both sulfide, such as mercaptans, such as TBM, and DMS, at least can be simultaneously carried out effectively with one desulfurizing plant. Sulfide, such as DMS, is received in that case. As a high adsorbent of especially adsorption capacity "X" type, If the adsorbent which makes it come to support one sort or two sorts or more of transition metals chosen as either zeolite of Y mold and beta mold from Ag, Cu, Zn, Fe, Co, and nickel according to the ion exchange" is used In addition to the ability to carry out the adsorption treatment of both the sulfur compounds of these mercaptans and sulfide that it is simultaneous and more efficiently, sulfur compounds, such as thiophenes or a hydrogen sulfide, are also effectively removable simultaneously.

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TECHNICAL FIELD

[Field of the Invention] This invention relates to the approach of carrying out adsorption treatment of the desulfurizing plant for carrying out adsorption treatment of the sulfur compound in fuel gas, such as a desulfurizing plant of fuel gas and the desulfurization approach, i.e., town gas, and LP gas, and the sulfur compound in these fuel gas, and desulfurizing fuel gas.

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PRIOR ART

[Description of the Prior Art] It is used as fuels, such as industrial use and home use, and also gas, such as low-grade hydrocarbon gas, such as methane, ethane, ethylene, a propane, and butane, or natural gas containing these, town gas, and LP gas, is used as a raw material for manufacture of the hydrogen used as the fuel for fuel cells, a controlled atmosphere, etc. In the steam reforming process which is one of the industrial manufacture approaches of hydrogen, under existence of catalysts, such as nickel system and Ru system, a steam is added, those low-grade hydrocarbon gas is reformed, and the reformed gas which uses hydrogen as a principal component is generated.

[0003] As odorant aiming at leakage security, sulfur compounds, such as sulfide, and thiophenes or mercaptans, are contained in fuel gas, such as town gas and LP gas. Specifically, they are tertiary butyl mercaptan (similarly it is called TBM for short), an isopropyl mercaptan, a normal propyl mercaptan, tertiary amyl mercaptan, a tertiary heptyl mercaptan, methyl mercaptan, ethyl mercaptan, etc. as tetrahydrothiophene (similarly it is called THT for short) and mercaptans as sulfide as dimethyl sulfide (it calls for short the inside DMS of this description), ethyl methyl sulfide, diethyl sulfide, and thiophenes.

[0004] Many DMS, THT, and TBM are used as odorant generally added, and each of the concentration is several ppm. In town gas, the case using both DMS and TBM is almost especially the case. For example, poisoning of the catalyst used with said steam reforming process will be carried out with these sulfur compounds, and it will cause performance degradation. For this reason, it is necessary to remove those sulfur compounds in fuel gas from fuel gas beforehand. Moreover, as for the amount of the residual sulfur compound, it is desirable for the residual sulfur compound also of little ** rare ***** to be low concentration as much as possible even if in the fuel gas which removed the sulfur compound.

[0005] Conventionally, the hydrodesulfurization process and the approach by the adsorbent are learned as the clearance approach of the sulfur compound contained in fuel gas. although add hydrogen to fuel gas, make a sulfur compound disassemble into a hydrogen sulfide under existence of catalysts, such as a Co-Mo system catalyst, and the hydrogen sulfide which is a decomposition product is made to stick to devulcanizing agents, such as a zinc oxide and an iron oxide, and being desulfurized, addition and heating of hydrogen are required of a hydrodesulfurization process -- etc. -- desulfurization actuation is dramatically complicated. On the other hand, the approach by the adsorbent is the approach of making adsorb a sulfur compound and removing by making the adsorbent which uses activated carbon, a metallic oxide, or a zeolite as a principal component pass fuel gas.

[0006] Although there is also an approach to which the adsorption capacity force is made to increase by heating among the approaches by the adsorbent, since a system becomes simpler [direction] making it adsorb in ordinary temperature, it is desirable. Since the method of removing a sulfur compound in ordinary temperature using an adsorbent needs neither heat nor hydrogen like a hydrodesulfurization process or a heating adsorption process, it is the simple desulfurization approach. This adsorbent is filled up with and used for a desulfurization container as shown in drawing 1 . However, since it becomes impossible to remove the sulfur compound in gas when an adsorbent is saturated with the sulfur compound by which this was adsorbed,

playback and exchange are required. Therefore, since the initial component of an adsorbent and exchange frequency will be greatly influenced by the size of the adsorption capacity force of an adsorbent, an adsorbent which has the higher adsorption capacity force is desired.

[0007] Since the ordinary temperature desulfurization process using adsorbents, such as activated carbon, and a manganese dioxide, a zeolite, only lets fuel gas pass to an adsorbent, it is a very simple approach. However, in the case of the adsorbent of these existing, especially the engine performance is influenced by the property of a sulfur compound. That is, the existing ordinary temperature adsorbents, such as activated carbon, and a manganese dioxide, a zeolite, do not have the enough adsorption engine performance, and its adsorption engine performance of sulfide, such as DMS, is especially low.

[0008] Various adsorbents are proposed as an adsorbent of the sulfur compound in gas until now. For example, in JP,6-306377,A, the mercaptans which are the odorization components of fuel gas, such as town gas and LP gas, are selectively said that polyvalent metal ion-exchange zeolites other than hydrogen and/or alkaline earth metal remove under an anoxia ambient atmosphere, a zeolite here is used regardless of the class, and it is supposed that Mn, Fe, Co, nickel, Cu, Sn, and Zn are desirable as polyvalent metal ion. The sulfur compounds for adsorption in this technique are only the easy mercaptans of adsorption, and the check of that adsorption capacity is performed by introducing 350 ppm TBM (town gas balance) into the sampling bag which put the above-mentioned zeolite into that example as the publication.

[0009] Moreover, in the manufacture process or a supply process, the case where the moisture of a minute amount is contained is in fuel gas. Although the selectivity which is not concerned with the existence of the moisture in fuel gas, but adsorbs a sulfur compound is required, in the conventional adsorbent, nothing is considered about this point including the adsorbent of the above-mentioned official report. In addition, about sulfide, such as mercaptans, such as TBM used as odorant in many cases, and DMS, since it is harder to adsorb in sulfide, such as DMS, especially in the conventional adsorbent, it becomes very important to make the amount of adsorption of sulfide, such as DMS, increase.

[0010] this invention person etc. is effective regardless of the class of sulfur compound, even if moisture is contained in fuel gas, as a result of pursuing about the adsorbent which functions still more effectively and continuing various experiments and examination from these many viewpoints, even if moisture was contained in fuel gas. Also about sulfide, such as DMS, the sulfur compound adsorbent in the fuel gas which has the outstanding adsorption capacity was developed previously, and it has applied [an application for patent 2000-23955 (application for patent 2000-232780), an application for patent 2000-123527, and an application for patent 2000-256493].

[0011] Although this adsorbent makes it come to support one sort or two sorts or more of transition metals chosen as the zeolite from Ag, Cu, Zn, Fe, Co, and nickel according to the ion exchange and has the adsorption engine performance regardless of the class of sulfur compounds, such as sulfide, thiophenes, and mercaptans, it has the adsorption engine performance which was especially excellent about sulfide, such as DMS. In this point, conventional activated carbon and a manganese dioxide, or a zeolite, since the adsorption engine performance of DMS is low, the above-mentioned adsorbent can be called unique adsorbent.

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EFFECT OF THE INVENTION

[Effect of the Invention] According to this invention, adsorption treatment of both the sulfur compounds in the fuel gas which contains both sulfide, such as mercaptans, such as TBM, and DMS, at least can be simultaneously carried out effectively with one desulfurizing plant. Sulfide, such as DMS, is received in that case. As a high adsorbent of especially adsorption capacity "X" type, If the adsorbent which makes it come to support one sort or two sorts or more of transition metals chosen as either zeolite of Y mold and beta mold from Ag, Cu, Zn, Fe, Co, and nickel according to the ion exchange" is used In addition to the ability to carry out the adsorption treatment of both the sulfur compounds of these mercaptans and sulfide that it is simultaneous and more efficiently, sulfur compounds, such as thiophenes or a hydrogen sulfide, are also effectively removable simultaneously.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] This invention aims at offering the approach of being more [being simultaneous and] efficient, carrying out adsorption treatment of the sulfide, such as mercaptans, such as TBM, and DMS, out of a desulfurizing plant as it is more [being simultaneous and] efficient in sulfide, such as mercaptans, such as fuel gas, such as town gas, and LP gas, natural gas, to TBM, and DMS, and comes to carry out adsorption treatment, and these fuel gas, and desulfurizing fuel gas by using the above data.

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MEANS

[Means for Solving the Problem] This invention is the desulfurizing plant of (1) sulfur-compound content fuel gas. In a desulfurization container The desulfurizing plant of the fuel gas characterized by coming to fill up with the upstream and downstream the adsorbent with which sulfur compound adsorption capacity differs is offered. Moreover, this invention is the desulfurizing plant of (2) sulfur-compound content fuel gas, and the desulfurizing plant of the fuel gas characterized by mixing two or more sorts of adsorbents with which sulfur compound adsorption capacity differs in a desulfurization container, and coming to be filled up is offered.

[0014] The desulfurizing plant of the fuel gas characterized by this invention being the desulfurizing plant of (3) sulfur-compound content fuel gas, and coming to fill up the sulfur compound adsorbent which makes it come to support one sort or two sorts or more of transition metals which filled up the upstream with the existing sulfur compound adsorbent into the desulfurization container, and were chosen as the zeolite from Ag, Cu, Zn, Fe, Co, and nickel by the downstream according to the ion exchange is offered.

[0015] The desulfurizing plant of the fuel gas characterized by this invention mixing the sulfur compound adsorbent which makes it come to support one sort or two sorts or more of transition metals which are the desulfurizing plants of (4) sulfur-compound content fuel gas, and were chosen as an existing sulfur compound adsorbent and an existing zeolite from Ag, Cu, Zn, Fe, Co, and nickel into the desulfurization container according to the ion exchange, and coming to be filled up is offered.

[0016] Moreover, this invention is the desulfurization approach of sulfur compound content fuel gas, and offers the desulfurization approach of the fuel gas characterized by desulfurizing through this fuel gas to the desulfurizing plant of above-mentioned (1) - (4).

[0017]

[Embodiment of the Invention] In this invention, the desulfurizing plant which mixes the adsorbent with which it is filled up with the adsorbent with which sulfur compound adsorption capacity differs by the upstream and downstream in a desulfurization container in the flow direction of processed sulfur compound content fuel gas, or sulfur compound adsorption capacity differs, and it comes to fill up is used. And adsorption treatment of two or more sulfur compounds contained in fuel gas can be simultaneously carried out with one desulfurizing plant by making both adsorbents contact through sulfur compound content fuel gas into the desulfurizing plant filled up with both adsorbents in this way.

[0018] This invention is applied to desulfurization of the fuel gas which contains both sulfide, such as mercaptans, such as TBM, and DMS, at least especially. As a kind of the adsorbents with which the above-mentioned sulfur compound adsorption capacity in this invention differs, the existing sulfur compound adsorbents, such as metallic oxides, such as activated carbon and a manganese dioxide, or a zeolite, can be used, for example. Generally as for these adsorbents, high adsorption capacity is shown to a sulfur compound with the high boiling point. In Above TBM (64.4 degrees C of boiling points), and DMS (37.2 degrees C of boiling points), the adsorption capacity to TBM is high. Therefore, although metallic oxides, such as activated carbon which is the existing sulfur compound adsorbent, and a manganese dioxide, a zeolite, etc. are effective in adsorption of mercaptans, such as TBM, they are not effective in adsorption of sulfide, such as

DMS.

[0019] On the other hand, as other kinds of the adsorbent with which said sulfur compound adsorption capacity differs, the high adsorbent of especially adsorption capacity is used among the sulfur compounds in fuel gas to the sulfide of the sulfide, such as mercaptans, such as the specific component to which it is hard to stick, i.e., TBM etc., and DMS, such as DMS, with the above-mentioned existing sulfur compound adsorbent.

[0020] Although all will be used if it is the adsorbent which has such engine performance as a high adsorbent of especially adsorption capacity to sulfide, such as DMS, the sulfur compound adsorbent concerning the above-mentioned application for patent 2000-23955 (application for patent 2000-232780), an application for patent 2000-123527, and an application for patent 2000-256493 can be mentioned as the desirable example. These are previously developed by this invention persons.

[0021] The above-mentioned sulfur compound adsorbent is an adsorbent which makes a zeolite come to support one sort or two sorts or more of transition metals chosen from Ag, Cu, Zn, Fe, Co, and nickel according to the ion exchange, and all cannot be concerned with the moisture concentration in fuel gas, but, in addition to thiophenes, such as sulfide, such as mercaptans, such as TBM contained in fuel gas, and DMS, and THT, can remove a hydrogen sulfide etc. effectively. Especially the adsorbent that made Ag or Cu support also in these transition metals is effective. As a zeolite, an X type zeolite, Y mold zeolite, and beta mold zeolite are used preferably.

[0022] In order to manufacture the above-mentioned adsorbent, each transition metals chosen from Above Ag, Cu, Zn, Fe, Co, and nickel are made to support by the ion-exchange method to a zeolite first. The compound of these metals is dissolved in water and, specifically, it considers as a water solution. As a compound of each metal, in order to carry out the ion exchange to the cation of a zeolite, it dissolves in water and the metallic compounds with which a metal may exist as a metal ion are used among the water solution. The cation in a zeolite is made to exchange for these metal ions by contacting this water solution with the ** agitating method, ** impregnation method, ** flow method, etc., as shown in a zeolite and below-mentioned drawing 4. Subsequently, after washing with water etc., it dries and is obtained by calcinating if needed.

[0023] The above-mentioned adsorbent for sulfur compound clearance can apply one sort or two sorts or more of sulfur compounds of the above-mentioned sulfide in [various] fuel gas, thiophenes, and the mercaptans to carrying out adsorption treatment. In addition to these sulfur compounds, this adsorbent acts effective also in adsorption treatment, such as a hydrogen sulfide, but it has the adsorption capacity which was especially excellent about sulfide, such as DMS. For this reason, it can be used suitable to carry out adsorption treatment of these sulfur compounds from fuel gas, such as town gas and LP gas, especially.

[0024] in this invention, adsorption treatment of both sulfide, such as mercaptans, such as TBM contained in fuel gas, such as town gas, and DMS, can be carried out that it is simultaneous and more efficiently with one desulfurizing plant by using the high adsorbent of especially adsorption capacity to sulfide, such as above DMS, with said existing adsorbent (that is, the existing adsorbent -- doubling). The desulfurizing plant which comes to carry out mixed filling of the adsorbent with which the adsorbent with which sulfur compound adsorption capacity differs is filled up with the upstream and downstream into a desulfurization container as a desulfurizing plant, or sulfur compound adsorption capacity differs is used. Drawing 2 -3 are drawing showing the example of a mode of the desulfurizing plant of this invention.

[0025] Drawing 2 is the case of the desulfurizing plant which comes to fill up with the upstream and downstream two kinds of adsorbents with which sulfur compound adsorption capacity differs into a desulfurization container. Adsorbent A is an adsorbent (mercaptans adsorption-capacity >> sulfide adsorption capacity: > shows the superiority or inferiority of adsorption capacity, and the number shows extent of the superiority or inferiority.) which adsorbs mercaptans, such as TBM. the following -- being the same -- a desulfurization container Nakagami style side is filled up. Adsorbent B is an adsorbent (mercaptans adsorption capacity < sulfide adsorption capacity) which sticks to sulfide, such as DMS, and a desulfurization container Nakashita style side is filled up with it.

[0026] Although the above mentioned mode (drawing 2) is the so-called bilayer discrete type with which the upstream is filled up with Adsorbent A and it fills up the downstream with Adsorbent B In using "the adsorbent which makes a zeolite come to support one sort or two sorts or more of transition metals chosen from Ag, Cu, Zn, Fe, Co, and nickel according to the ion exchange" especially as an adsorbent B Even if only the case of the bilayer discrete type of restoration sequence "the adsorbent A-> adsorbent B" is effective and is the same bilayer discrete type, with the bilayer discrete type of restoration sequence "the adsorbent B-> adsorbent A", the effectiveness of this invention is not acquired from the upstream. Although this reason is unknown, in the bilayer discrete type of the adsorbent A-> adsorbent B, it is thought that a certain different significant absorption from the absorption in the bilayer discrete type of the adsorbent B-> adsorbent A has occurred.

[0027] Drawing 3 is the case of the desulfurizing plant which mixes two or more sorts of adsorbents with which sulfur compound adsorption capacity differs, and it comes to fill up into a desulfurization container. Adsorbent A is an adsorbent (mercaptans adsorption capacity < sulfide adsorption capacity) which sticks to sulfide, such as DMS, and into a desulfurization container, the adsorbent (mercaptans adsorption capacity >> sulfide adsorption capacity) which adsorbs mercaptans, such as TBM, and Adsorbent B mix both adsorbents, and are filled up with it. Stainless steel, glass, various plastics, etc. are mentioned that what is necessary is just the ingredient which is not invaded by processed fuel gas as a component of the desulfurization container of this invention.

[0028] In these desulfurizing plants, as an adsorbent B, if the sulfur compound adsorbent which makes it come to support one sort or two sorts or more of transition metals chosen from Ag, Cu, Zn, Fe, Co, and nickel according to the ion exchange is used for the zeolite of either a zeolite especially said X type zeolite, Y mold zeolite and beta mold zeolite, in addition to mercaptans and sulfide, adsorption treatment also of the sulfur compounds, such as thiophenes and a hydrogen sulfide, can be simultaneously carried out to it from fuel gas. Although the existing sulfur compound adsorbents, such as metallic oxides, such as activated carbon and a manganese dioxide, or a zeolite, are used as an adsorbent A, for example in that case, activated carbon is used especially preferably.

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EXAMPLE

[Example] Hereafter, although this invention is explained in more detail based on an example, of course, this invention is not restricted according to these examples.

[0030] <preparation of a sample offering adsorbent> — the Na-X mold zeolite (the TOSOH CORP. make —) of marketing as a zeolite trade name: — F9-HA and SiO₂/aluminum₂O₃ ratio (the same a mole ratio and the following) — =2.5 — a commercial H-beta mold zeolite (the TOSOH CORP. make and trade name:HSZ — 930 HOD) SiO₂/aluminum₂O₃ ratio — =27.4 and a commercial Na-Y mold zeolite (the TOSOH CORP. make —) trade name: — HSZ320NAD and SiO₂/aluminum₂O₃ ratio — =5.7 — a commercial H-Y mold zeolite (the TOSOH CORP. make and trade name:HSZ — 320 HOD) SiO₂/aluminum₂O₃ ratio — =5.6 and a H-USY mold zeolite (the TOSOH CORP. make —) trade name: — HSZ360HUD and SiO₂/aluminum₂O₃ ratio — =13.7 — The K-L mold zeolite (the TOSOH CORP. make, trade name:HSZ500KOD, SiO₂/aluminum₂O₃ ratio = 6.0) and Na-mordenite mold zeolite (the TOSOH CORP. make, trade name:HSZ642NAD, SiO₂/aluminum₂O₃ ratio = 18.3) were used.

[0031] These zeolites are fabricated on a cylindrical pellet (the diameter of 1.5mm, die length = 3-4mm), using an alumina or about clay 20wt% as a binder. On the other hand, a silver nitrate, copper acetate, etc. were dissolved in distilled water, and the water solution of each metal salt was obtained. By the various ion-exchange approaches shown in drawing 4 using the water solution of each [these] metal salt, after making each cation in the above-mentioned zeolite (Na⁺, K⁺, or H⁺) exchange for Ag ion, Cu ion, Zn ion, Fe ion, Co ion, and nickel ion, distilled water (inside DIW of drawing 4) washed 5 times, and, subsequently it dried and calcinated.

[0032] These results are collectively shown in a table 1. Among a table 1, although the code shows to the column of a sample name, among this column, although "Ag(Na)-Y" made the Na-Y mold zeolite support Ag according to the ion exchange, it is semantics, and the same is said of this point, a table 2, and the following publications. In addition, desiccation and baking conditions are common, and each sample performed desiccation at 100 degrees C into air on the 1st, and performed baking at 400 degrees C into desiccation nitrogen for 2 hours. In this way, each sample offering adsorbent which made various zeolites support a metal according to the ion exchange was obtained.

[0033]

[Table 1]

サンプル名	ゼオライト重量 /g	試薬	試験 /g	蒸留水 /g	イオン交換方法
Ag(Na)-Y	30	硝酸銀	22.9	500	攪拌法
Ag(CD)-Y	50	硝酸銀	31.1	500	流通法
Ag(Na)-X	75	硝酸銀	30.6	800	攪拌法
Ag(CD)-β	30	硝酸銀	11.0	150	含浸法
Cu(CD)-Y	75	酢酸銅1水和物	20.5	800	攪拌法
Cu(Na)-X	75	酢酸銅1水和物	17.9	800	攪拌法
Cu(CD)-β	30	酢酸銅1水和物	6.9	150	含浸法
Zn(CD)-β	30	硫酸亜鉛7水和物	9.4	150	含浸法
Fe(CD)-β	30	硫酸鉄7水和物	4.8	500	攪拌法
Co(CD)-β	30	酢酸コバルト4水和物	4.4	150	含浸法
Ni(CD)-β	30	酢酸ニッケル4水和物	4.4	150	含浸法
Na(CD)-β	30	塩化ナトリウム	20.3	500	攪拌法
Ag(CD)-USY	50	硝酸銀	14.4	500	流通法
Ag(CD)-L	30	硝酸銀	21.9	500	攪拌法
Ag(Na)-Mor	30	硝酸銀	8.5	150	含浸法

[0034] <An example 1 - the examples 1-17 of 13:comparison> (sulfur compound adsorption test 1)

The adsorption test of a sulfur compound was carried out using the testing device shown in drawing 5. The packed tube (cylinder coil) was filled up with each sample offering adsorbent obtained above among drawing 5, and the adsorption test of a sulfur compound was carried out about each. The test condition was carried out as follows. Packed tube: 28.4mm(diameter) x63.2mm (height) and this were filled up with 340cm of each sample offering adsorbent. trial gas: -- town gas [13A:methane ** 87.8% (the same, when it cannot touch capacity % and especially the following) Ethane **5.9%, propane **4.6%, n-butane **0.8%, and i-butane **0.8%], sulfur compound concentration [in trial gas]: -- 4.4 mg-SNm3 (DMS=50wt% --) This added 380 ppm (-30 degrees C of dew-points) of **** TBM=50wt% in this gas equivalent to DMS=1.8ppm (it is the same capacity ppm and the following) and TBM=1.2ppm (based on underwater bubbling of the trial gas in the inside of a thermostat). Gas rate: 340 L/h, LV(linear velocity of gas) =15 cm/sec, SV(space velocity) =8500h-1, a temperature:room temperature (20 degrees C), pressure:ordinary pressure. This adsorption test was altogether carried out on the same equipment and the same conditions including the example of a comparison.

[0035] The amount of adsorption of the sulfur compound by each sample offering adsorbent was carried out as follows, and was calculated. By the above-mentioned test condition, trial gas was introduced from the packed tube inlet port, the gas discharged from a packed tube outlet was sampled with time, and it asked for the concentration of a sulfur compound by GC-FPD (gas chromatograph with a flame photometric detector). The amount of adsorption of a sulfur compound integrates the total sulfur compound amount of adsorption of the event of each sulfur compound concentration in a packed tube outlet amounting to 0.1 ppm, and computes it as the sulfur amount of adsorption by the following formula (1). The same is said of this point and the following examples.

[0036]

[Formula 1]

$$\text{硫黄吸着量 (wt\%)} = \frac{\text{吸着した硫黄化合物中の硫黄量 (g)}}{\text{吸着剤の重量 (g)}} \times 100 \quad (1)$$

[0037] A table 2 is as a result of the above-mentioned adsorption test. The result of having made it the same with the above and having performed the adsorption test about the various porous materials considered having the various adsorbents and absorption of marketing besides the various commercial zeolite itself as an example of a comparison is also shown in a table 2.

[0038]

[Table 2]

例番号	サンプル名	担持材料	Si/Al ₂	吸着剤名(商品名等)	担持元素	硫黄吸着量
実施例1	Ag(Na)-Y	Na-Y型ゼオライト	5.7	HS2320KAD	東ソー	4.10wt%
実施例2	Ag(O)-Y	H-Y型ゼオライト	5.6	HS2320HOD	東ソー	1.91wt%
実施例3	Ag(Na)-X	Na-X型ゼオライト	2.5	F9-HA	東ソー	1.78wt%
実施例4	Ag(O)-β	H-β型ゼオライト	27.4	HS2390HOD	東ソー	1.70wt%
実施例5	Ag(O)-USY	H-USY型ゼオライト	13.7	HS2360HOD	東ソー	0.34wt%
実施例6	Ag(O)-L	K-L型ゼオライト	6.0	HS2500KOD	東ソー	0.19wt%
実施例7	Ag(Na)-Mor	Na-モルデナイト型ゼオライト	18.3	HS2642KAD	東ソー	0.46wt%
実施例8	Cu(O)-Y	H-Y型ゼオライト	5.6	HS2320HOD	東ソー	1.17wt%
実施例9	Cu(O)-β	H-β型ゼオライト	27.4	HS2390HOD	東ソー	1.10wt%
実施例10	Zn(O)-β	H-β型ゼオライト	27.4	HS2390HOD	東ソー	0.24wt%
実施例11	Fe(O)-β	H-β型ゼオライト	27.4	HS2390HOD	東ソー	0.14wt%
実施例12	Co(O)-β	H-β型ゼオライト	27.4	HS2390HOD	東ソー	0.14wt%
実施例13	Ni(O)-β	H-β型ゼオライト	27.4	HS2390HOD	東ソー	0.13wt%
比較例1	Na-Y	Na-Y型ゼオライト	5.7	HS2320HAD	東ソー	<0.01wt%
比較例2	H-Y	H-Y型ゼオライト	5.6	HS2320HOD	東ソー	0.05wt%
比較例3	Na-X	Na-X型ゼオライト	2.5	F9-HA	東ソー	0.23wt%
比較例4	H-β	H-β型ゼオライト	27.4	HS2390HOD	東ソー	0.06wt%
比較例5	Na-β	H-β型ゼオライト	27.4	HS2390HOD	東ソー	0.04wt%
比較例6	H-USY	H-USY型ゼオライト	13.7	HS2360HOD	東ソー	<0.01wt%
比較例7	K-L	K-L型ゼオライト	6.0	HS2500KOD	東ソー	<0.01wt%
比較例8	Na-Mor	Na-モルデナイト型ゼオライト	18.3	HS2642HAD	東ソー	0.01wt%
比較例9	H-Mor	H-モルデナイト型ゼオライト	15.0	HS2620HOD	東ソー	<0.01wt%
比較例10	活性炭	活性炭(ハロゲン吸着用)		XRC824	武田薬品	0.03wt%
比較例11	活性炭	活性炭(硫黄吸着用)		TAC824	武田薬品	0.03wt%
比較例12	活性炭	活性炭(付臭剤吸着用)		SRCA	武田薬品	0.07wt%
比較例13	金属酸化物	ZnO		C7-2	東洋CCI	—
比較例14	アルミナ	活性アルミナ		KH012	住友化学	0.01wt%
比較例15	アルミナ	活性アルミナ		KH012	住友化学	—
比較例16	シリカ	シリカゲル		A型	富士シリシア化学	0.08wt%
比較例17	シリカ	シリカゲル		B型	富士シリシア化学	<0.01wt%

(備考) ①Si/Al₂はSiO₂/Al₂O₃モル比。②硫黄吸着量の欄で「—」のものは、試験開始直後から硫黄化合物の吸着が開始したもので、実質上硫黄化合物の吸着能はないことを示している。

[0039] As a table 2, in a thing with a commercial zeolite (examples 1-9 of a comparison), even if the sulfur amount of adsorption is good, it is 0.23wt(s)%. Moreover, about adsorbents other than a commercial zeolite (examples 10-17 of a comparison), it is lower than it. That is, if adsorbents, such as a commercial zeolite and activated carbon, remain as they are, they show that it is not useful as an adsorbent of the sulfur compound in the fuel gas containing moisture.

[0040] On the other hand, although examples 1-13 are the cases where a commercial zeolite is made to support transition metals, such as Ag, Cu, Zn, Fe, Co, and nickel, according to the ion exchange, compared with the thing with a commercial zeolite, the sulfur adsorption engine performance is improved effectively. Especially the sulfur amount of adsorption at the time of making an X type zeolite, Y mold zeolite, and beta mold zeolite support silver or copper according to the ion exchange (examples 1-4, 8-9) exceeds 1wt%, and shows the very effective adsorption property. Especially the sulfur amount of adsorption at the time of making a Na-Y mold zeolite support Ag according to the ion exchange especially (example 1) indicates the outstanding adsorption property to be 4.1wt(s)%. Although 1.8 ppm and 1.2 ppm of TBM are contained in trial gas for DMS and about 380 ppm of water are contained in it, DMS and TBM are effectively adsorbed under coexistence of such moisture.

[0041] <Example 14> (sulfur-compound adsorption test 2: adsorption performance test classified by class of a sulfur compound)

The following adsorbent A and Adsorbent B were prepared as an adsorbent.

Adsorbent A: Commercial activated carbon for desulfurization (the Takeda Chemical Industries, Ltd. make, the granular egret NCC)

Adsorbent B: The adsorbent of an example 1 (what carried out the ion exchange of the complex ion to the Na-Y mold zeolite in the silver-nitrate water solution)

Using the testing device shown in drawing 5, tales-doses restoration of these adsorbents A and the adsorbent B was carried out at the packed tube [a quartz tube with a bore of 8mm (inner diameter)], respectively, and the adsorption test was carried out for every class of sulfur compound. Adsorbent B was filled up with what ground the pellet of the cylindrical shape obtained above <preparation of a sample offering adsorbent>, and carried out the particle size regulation to the range of 0.35 to 0.71mm three times 1.0cm. The particle size regulation of the

adsorbent A was carried out to the same particle size, and it was used for it. As trial gas, each gas which carried out about 1000 ppm (-20 degrees C of dew-points) addition of the water was used for each gas (respectively 10 ppm, N2 balance) which diluted DMS, TBM, THT, CS2, H2S, and CH3SH with nitrogen, respectively. The gas flow rate set to 1000cm³/min (SV=60000h⁻¹), sampled the gas of an adsorbent layer outlet side with time, measured it with the fixed time interval by GC-FPD, and asked for the concentration of each sulfur compound.

[0042] Drawing 6 is as a result of the above-mentioned adsorption test. It turns out as drawing 6 that the sulfur adsorption engine performance of Adsorbent B is excellent compared with the sulfur adsorption engine performance of Adsorbent A. the adsorption engine performance which especially the adsorbent A boiled Adsorbent B markedly to not being [to which it sticks slightly] alike too much (sulfur amount of adsorption = 0.7wt%), and was excellent about DMS is shown (sulfur amount of adsorption = 4.9wt%). About TBM, although it is a both **** EQC, Adsorbent B shows [SH / THT, H2S, and / CH3] the adsorption engine performance which was excellent compared with Adsorbent A.

[0043] <Example 15> (sulfur compound adsorption test 3: adsorption performance test of TBM and DMS)

About same Adsorbent A and same Adsorbent B as having used in the example 14, the breakthrough situation according to sulfur compound of TBM and DMS was measured. As trial gas, the gas which carried out about 1000 ppm (-20 degrees C of dew-points) addition of the water was used for the gas (DMS=5ppm, TBM=5ppm, N2 balance) which diluted TBM and DMS with nitrogen. The gas flow rate set to 1000cm³/min (SV=60000h⁻¹), sampled the gas of an adsorbent layer outlet side with time, measured it with the fixed time interval by GC-FPD, and asked for the concentration of TBM and DMS.

[0044] Drawing 7 is as a result of this adsorption test. Drawing 7 (a) Time amount until a breakthrough appears about TBM has long Adsorbent A compared with Adsorbent B as - (b). On the other hand, to carrying out a breakthrough at the time of about 300-minute progress, with Adsorbent B, a breakthrough does not appear till about 1200-minute progress, but the adsorption engine performance is maintained about DMS with Adsorbent A.

[0045] <Example 16> (sulfur-compound adsorption test 4: the method [Adsorbent / C / Adsorbent A, Adsorbent B, or] of restoration adsorption performance test by how)

The following adsorbent A, Adsorbent B, and Adsorbent C were prepared as an adsorbent.

Adsorbent A: Commercial activated carbon for desulfurization (the Takeda Chemical Industries, Ltd. make, the granular egret NCC)

Adsorbent B: The adsorbent of an example 1 (what carried out the ion exchange of the complex ion to the Na-Y mold zeolite in the silver-nitrate water solution)

Adsorbent C: The adsorbent of an example 4 (what carried out the ion exchange of the complex ion to the H-beta mold zeolite in the silver-nitrate water solution)

[0046] The adsorption test was carried out using the desulfurizing plant which changed and constituted the method [Adsorbent / in a desulfurization container / Adsorbent A, Adsorbent B, or Adsorbent C] of restoration. Drawing 8 is drawing showing restoration of the adsorbent A in the desulfurization container used by this adsorption test, and Adsorbent B, and arrangement relation. About Adsorbent C, it is the same as restoration of Adsorbent B, and arrangement relation. For drawing 8 (a), drawing 8 (c) is the desulfurizing plant (single component type: example of a comparison) filled up only with one kind each of Adsorbent A and Adsorbent B, the desulfurizing plant (bilayer discrete type: example) with which drawing 8 (b) was filled up with Adsorbent A and Adsorbent B one by one from the fuel gas entrance side, and the desulfurizing plant which mixed Adsorbent A and Adsorbent B and was filled up.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] Drawing showing the conventional ordinary temperature desulfurizing plant

[Drawing 2] Drawing showing the example of a mode of the desulfurizing plant of this invention

[Drawing 3] Drawing showing the example of a mode of the desulfurizing plant of this invention

[Drawing 4] Drawing showing the various ion-exchange approaches used in the example

[Drawing 5] Drawing showing the outline of the testing device used in the example

[Drawing 6] Drawing showing the result of an example 14 (sulfur-compound adsorption test 2: adsorption performance test classified by class of a sulfur compound)

[Drawing 7] Drawing showing the result of an example 15 (sulfur compound adsorption test 3: adsorption performance test of TBM and DMS)

[Drawing 8] Drawing showing the desulfurizing plant used in the example 16 (sulfur-compound adsorption test 4: the method of restoration of Adsorbent A and Adsorbent B adsorption performance test by how)

[Drawing 9] Drawing showing the result of an example 16 (sulfur-compound adsorption test 4: the method of restoration of Adsorbent A and Adsorbent B adsorption performance test by how)

[Drawing 10] Drawing showing the result at the time of carrying out mixed filling of Adsorbent A and the adsorbent C into a desulfurization container

[Translation done.]

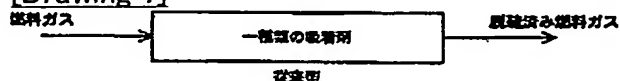
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DRAWINGS

[Drawing 1]



[Drawing 2]



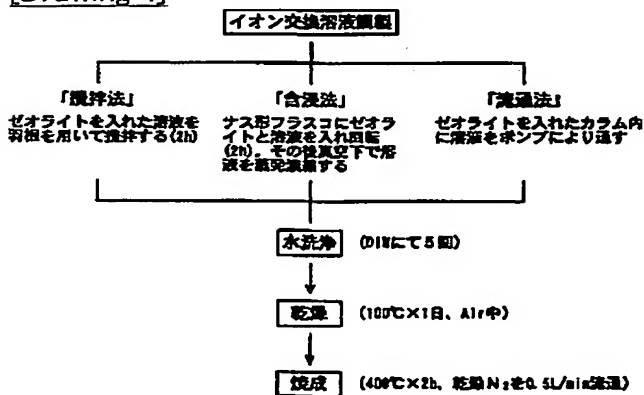
吸着剤A = TBS等のメルカプタン類を吸着する吸着剤
(メルカプタン類吸着能 >> サルファイド類吸着能)
吸着剤B = DBF等のサルファイド類を吸着する吸着剤
(メルカプタン類吸着能 < サルファイド類吸着能)

[Drawing 3]

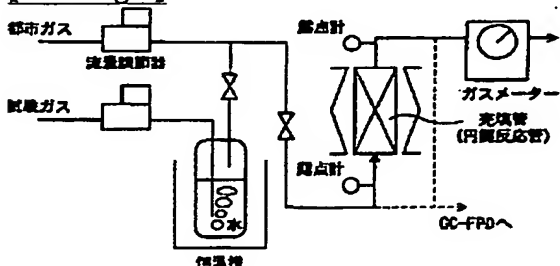


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(メルカプタン類吸着能 >> サルファイド類吸着能)
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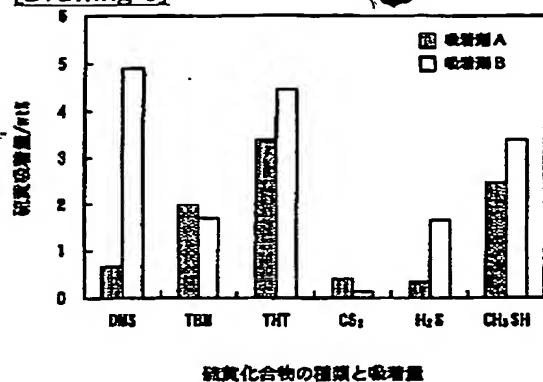
[Drawing 4]



[Drawing 5]

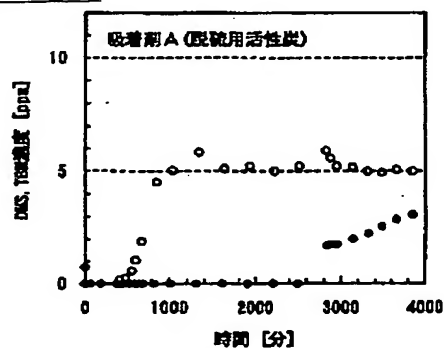


[Drawing 6]

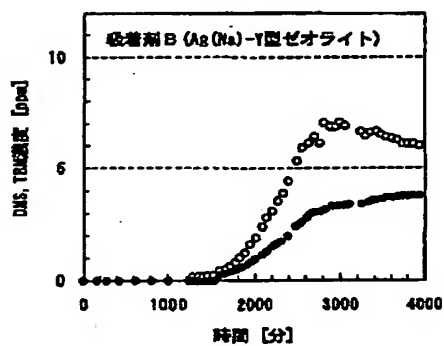


[Drawing 7]

(a)



(b)



吸着層出口での有機化合物濃度

原料ガス:

TBM 5ppm

DMS 5ppm

H₂O 1000ppm

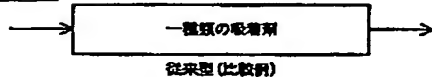
N₂ バランス

○ DMS

● TBM

[Drawing 8]

(a)



(b)



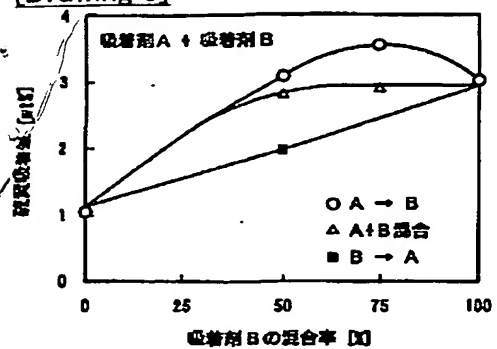
(c)



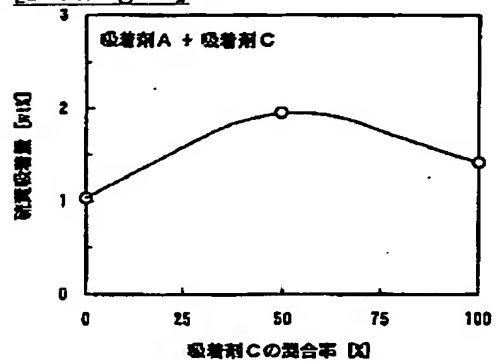
(d)



[Drawing 9]



[Drawing 10]



[Translation done.]